

A phenomenology for multiple phases in the heavy fermion skutterudite superconductor $\text{PrOs}_4\text{Sb}_{12}$

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The two superconducting phases recently discovered in skutterudite $\text{PrOs}_4\text{Sb}_{12}$ are discussed by using the phenomenological Ginzburg-Landau theory based on the the cubic (tetrahedral) crystal symmetry T_h . Building on experimental input coming from the recent thermal conductivity measurements, the structure of the gap functions for these two phases are considered for the spin singlet pairing case. One of the phases, lying in the high temperature and high field region (A-phase) is a strongly "anisotropic s -wave" state, whereas the other phase (B-phase) is an "anisotropic $s + id$ -wave" state. The B-phase breaks cubic crystal symmetry and time reversal symmetry spontaneously. The cubic symmetry breaking in B-phase causes anomalous crystal strains which could be seen in the anisotropy of thermal expansions and isothermal elastic constants. As a signal of the time reversal symmetry breaking, it is expected that an internal spontaneous magnetization should be observed by the μSR measurement.

I. INTRODUCTION

Recently, heavy fermion superconductivity was discovered at 1.85 K in the skutterudite compound $\text{PrOs}_4\text{Sb}_{12}$ with a cubic (tetrahedral) crystal symmetry T_h [1]. Intriguingly, it was indicated that there are multiple superconducting phases in this material, like in the Uranium compounds [2,3]. Two specific heat jumps were observed at $T_{c1} = 1.85\text{ K}$ and $T_{c2} = 1.75\text{ K}$ in the absence of the magnetic field [4]. Moreover, the thermal conductivity measurement in a magnetic field rotated relative to the crystal axes reveals a novel change in the symmetry of the gap function in the ab -plane [5]. The result was that the gap function has four point-node-like structure (four dips) in the $[100]$ and $[010]$ directions on the Fermi surface in the high field and high temperature region (A-phase), and two dips in the $[010]$ direction in the low field and low temperature region (B-phase). The proposed phase diagram is given in Fig. I. Unfortunately, the gap structure along the c -axis remains unresolved within the presently available data [5], and one of the purpose of this paper is to consider this problem. The presence of the point node like structures appears to be consistent with the power law behavior of the specific heat [1,4] and the nuclear-spin-lattice relaxation [6] at low temperatures (See also Ref. [7]). Another evidence for the double superconducting transition is the thermal expansion measurement along $[100]$ direction [8]; two clear jumps are observed at around $T_{c1} = 1.85\text{ K}$ and $T_{c2} = 1.75\text{ K}$ in the absence of the magnetic field (Fig. I).

In this paper, the symmetry of the gap functions for A- and B-phase are discussed by use of a phenomenological Ginzburg-Landau (GL) theory [2] based on the tetrahedral crystal symmetry T_h . At present, there are no information as to whether the superconductivity is spin singlet or spin triplet pairing. Only the singlet pair-

ing case will be discussed in this paper. The gap structure along the c -axis is considered. We find that the gap function appears to have two additional dips along the c -axis in A-phase (in total there are six dips, along the $[100]$, $[010]$ and $[001]$ directions), while no additional dips are inferred for the B-phase resulting in a total of two dips, along the $[010]$ direction). The A-phase gap is essentially an "anisotropic s -wave" state and the B-phase gap is an "anisotropic $s + id$ -wave" state. The B-phase gap breaks the cubic crystal symmetry and time reversal symmetry spontaneously, from which one can expect a crystal deformation with cubic symmetry breaking to occur in this phase. To verify this, the phenomenological strain-order parameter coupling is taken into account and the thermal expansions and isothermal elastic constants are calculated [9]. One finds that these values become anisotropic in B-phase.

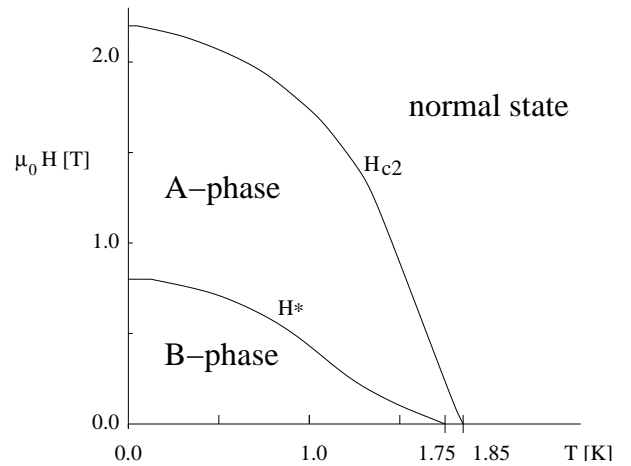


FIG. I. A rough sketch of the phase diagram proposed by Izawa et. al [5]. See, also Refs. [4] and [8].

The pairing mechanism for this superconductivity should be also interesting. It is widely believed that the mechanism for the heavy fermion superconductivity in the Uranium compounds comes from magnetic interactions, but $\text{PrOs}_4\text{Sb}_{12}$ is a non-magnetic compound. Several experiments indicate that the ground state of Pr $4f$ -electrons in the crystalline electric field would most likely be the non-Kramers doublet Γ_3 state [1,4,7]. The Γ_3 ground state has quadrupolar fluctuations and its relations to the heavy fermion behavior [10] and also to a pairing mechanism seems to be possible to discuss. However, its relation to the pairing symmetry, which will be focused in this paper, is unclear at present. Moreover, the singlet Γ_1 state without quadrupolar fluctuations is also proposed as the ground state [11]. The details of the pairing mechanism will not be discussed here.

The organization of this paper is as follows. In section II, the gap structures for the A- and B-phases are discussed. In section III, jumps of the specific heat at two transition points (T_{c1} and T_{c2}) are calculated. To fit these calculations to the specific heat measurement [4], one obtains information for the coefficients of the fourth order terms in the GL potential. In section IV, arguments for a spontaneous cubic symmetry breaking in the B-phase are presented, and a summary is given in section V.

II. THE GAP STRUCTURES

In this section, the gap structures for the A- and B-phases in the spin singlet pairing case are discussed within the framework of the phenomenological GL theory. Information on the gap structure along the c -axis, which is still unresolved by the thermal conductivity measurement [5], are obtained.

The GL theory to be considered is based on the cubic crystal symmetry group T_h . This group has essentially three irreducible representations A_1 (Γ_1), E (Γ_2, Γ_3) and T (Γ_5).

A. A-phase

In this phase, four point-node-like (four-dip) structures of the gap function located within the ab -plane are observed along the $[100]$ and $[010]$ directions [5]. Then, the question is whether the gap function has two additional dips along c -axis (i.e. the gap has a total of six dips) or not (i.e. four dips in all).

It should be pointed out that H_{c2} is isotropic in this superconductor [5]. In general, the superconducting states represented by a multicomponent order parameter should have an anisotropic H_{c2} [2,3]. Therefore, the gap function in the A-phase appears to be represented by a single component order parameter, i.e., the A_1 representation.

The gap function with six dips along the $[100]$, $[010]$ and $[001]$ directions belongs to the A_1 representation because this structure has the cubic symmetry T_h . Actually, one can see this as follows. Let η and $\phi_s(\mathbf{k})$ stand for the order parameter and the basis function of the A_1 representation, respectively. By the definition, $\phi_s(\mathbf{k})$ should be invariant under T_h . The gap function in this representation is

$$\Delta(\mathbf{k}) = \eta \phi_s(\mathbf{k}).$$

The six-dip state can be represented by using invariants [12]:

$$\phi_s(\mathbf{k}) = s + k_x^4 + k_y^4 + k_z^4 \quad (s \simeq -1), \quad (1)$$

and also

$$\phi_s(\mathbf{k}) = s + k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2 \quad (s < -1), \quad (2)$$

... etc. are possible. When one takes $s = -1$ in Eq. (1) ($s = 0$ in Eq. (2)), the dips become point nodes. Gap functions such as in Eqs. (1) and (2) have been discussed in the context of the YNiB_2C_2 superconductor [13]. *It should be noted that the function $\phi_s(\mathbf{k})$ which can give rise to six dips is not limited to these two forms.* There are many possible forms which have six dips. The point is that the six-dip state can be described in the A_1 representation and essentially categorized into the so-called "anisotropic s -wave" state.

The four-dip state does not belong to the A_1 representation because this gap structure does not have the cubic symmetry. Actually, one would see in the next subsection that this state belongs to the $A_1 \oplus E$ combined representation [12]. Then, a multicomponent orderparameter is needed to describe this gap function (See, Eq. (4)), and in general, an anisotropy in H_{c2} is to be expected [2,3]. In contradiction to the experimental result [5]. Moreover, in the next subsection one would see that the four-dip structure arises in a somewhat accidental way (See, Eq. (5)).

Then, in the A-phase, it seems to be natural to consider that the six-dip state (strongly anisotropic s -wave state) is realized.

B. B-phase

In this phase, two dips of the gap function within in ab -plane along $[010]$ direction are observed [5]. Then, the question is whether the gap function has two additional dips along the c -axis (i.e. the gap has in total four dips) or not (i.e. a total of two dips).

Phase transitions are observed by varying H and also varying T without a magnetic field turned on (Fig. 1). To describe the phase transition without external fields,

one can consider the combined representations. Possible combinations in the present case are $A_1 \oplus E$, $A_1 \oplus T$, $E \oplus T$, and $A_1 \oplus E \oplus T$.

As we will see below, both the four-dip and two-dip states belong to the $A_1 \oplus E$ representation. Let g_{A_1} and g_E stand for the effective coupling constant of the pairing interaction for the A_1 channel and the E channel, respectively. In general, these values are split by the crystal field. The $A_1 \oplus E$ combined state is realized when [2,14]

$$g_{A_1} \simeq g_E, \quad (3)$$

is satisfied. This comes from some accidental degeneracy.

The gap function in $A_1 \oplus E$ model is expanded by the basis functions of A_1 and E representations:

$$\Delta(\mathbf{k}) = \eta \phi_s(\mathbf{k}) + \eta_1 \phi_{2y^2-z^2-x^2}(\mathbf{k}) + \eta_2 \phi_{z^2-x^2}(\mathbf{k}). \quad (4)$$

The function $\phi_{2y^2-z^2-x^2}(\mathbf{k})$ is the first component of the 2D basis of the E representation which transforms like the function $2k_y^2 - k_z^2 - k_x^2$ under the T_h group. It has two line nodes parallel to the ac -plane. The function $\phi_{z^2-x^2}(\mathbf{k})$ is the second component of the 2D basis of the E representation which transforms like the function $k_z^2 - k_x^2$ under the T_h group. It has two line nodes crossing at two points along the $[010]$ direction. Note that these functions may include terms beyond quadratic order in the momentum \mathbf{k} . However the nodal structure of these basis functions remain unaltered, in general, even if the higher order terms are included.

To obtain a four-dip state along the $[010]$ and $[001]$ directions, one must fine-tune the three basis functions into the particular forms $\phi_s(\mathbf{k}) = 1 - 2(k_x^4 + k_y^4 + k_z^4)/3$, $\phi_{2y^2-z^2-x^2}(\mathbf{k}) = 2k_y^4 - k_z^4 - k_x^4$, $\phi_{z^2-x^2}(\mathbf{k}) = \sqrt{3}(k_z^4 - k_x^4)$, where the second order terms of \mathbf{k} are absent, and also the three order parameters are fixed to take the particular values [12]

$$(\eta, \eta_1, \eta_2) \simeq (1, -\frac{1}{6}, \frac{1}{2\sqrt{3}}). \quad (5)$$

This looks highly accidental. The gap function with four dipoles along $[100]$ and $[010]$ directions discussed in the previous subsection can also be obtained in the same manner [12].

Two-dip state is realized when

$$(\eta, \eta_1, \eta_2) = (\alpha, 0, \pm i\beta), \quad \alpha, \beta \in \mathbf{R}, \quad (6)$$

because $\phi_{z^2-x^2}(\mathbf{k})$ is zero and $\phi_s(\mathbf{k})$ becomes minimum along $[010]$ direction. Note that the two-dip structure appears generically for all values of the two parameters α and β . Moreover, it is not necessary to fix the basal functions $\phi_s(\mathbf{k})$, $\phi_{2y^2-z^2-x^2}(\mathbf{k})$ and $\phi_{z^2-x^2}(\mathbf{k})$ to particular forms. The only assumption needed here is the six-dip structure of the function $\phi_s(\mathbf{k})$. It should be noted again that the function $\phi_s(\mathbf{k})$ is not limited to a particular form to obtain six dipoles. There are many possible

forms to obtain six dipoles and described in the A_1 representation (anisotropic s -wave state). Eq. (1) (or Eq. (2)) is one of the examples. Then, the state Eq. (6) is an anisotropic $s + id_{z^2-x^2}$ -wave state and breaks the cubic crystal symmetry and also the time reversal symmetry spontaneously.

Let us discuss the stability of these two states Eqs. (5) and (6). It will be shown that the state Eq. (6) is found as a stable state of the system, but the state Eq. (5) would be not.

Consider the GL potential for $A_1 \oplus E$ representation of T_h [14]

$$\begin{aligned} F_{\text{op}} = & A_{A_1}(T)|\eta|^2 + \beta|\eta|^4 + A_E(T)(|\eta_1|^2 + |\eta_2|^2) \\ & + \beta_1(|\eta_1|^2 + |\eta_2|^2)^2 + \beta_2(\eta_1\eta_2^* - \eta_1^*\eta_2)^2 \\ & + \theta_1|\eta|^2(|\eta_1|^2 + |\eta_2|^2) \\ & + \frac{\theta_2}{2}\{\eta^{*2}(\eta_1^2 + \eta_2^2) + c.c\}, \end{aligned} \quad (7)$$

where

$$A_{A_1}(T) = \frac{T}{T_{A_1}} - 1, \quad A_E(T) = \frac{T}{T_E} - 1,$$

and

$$T_{A_1} \sim \exp[-1/g_{A_1}N(0)], \quad T_E \sim \exp[-1/g_EN(0)],$$

in the weak coupling approximation (See. Eq. (3)). $N(0)$ is the density of states at the Fermi surface. We consider a temperature region $T < \min[T_{A_1}, T_E]$. The terms proportional to θ_1 and θ_2 denote the coupling between the order parameter in the A_1 representation and the two order parameters in the E representation. In general, another coupling term

$$\theta_3 [e^{i\gamma_3}\eta^*(\eta_1|\eta_1|^2 - 2\eta_1|\eta_2|^2 - \eta_1^*\eta_2^2) + c.c.]$$

could be included in the potential but this term makes the phase transition 1st order [14], which appears to be inconsistent with the specific heat experiments [1,4]. So, this term is excluded here. For simplicity, we take

$$\theta_1 = \theta_2. \quad (8)$$

By using the parameterization

$$\eta = |\eta|, \quad \eta_1 = |\tilde{\eta}| \cos \psi e^{i\phi_1}, \quad \eta_2 = |\tilde{\eta}| \sin \psi e^{i\phi_2},$$

Eq. (7) becomes

$$\begin{aligned} F_{\text{op}} = & A_{A_1}(T)|\eta|^2 + A_E(T)|\tilde{\eta}|^2 + \beta|\eta|^4 + \beta_1|\tilde{\eta}|^4 \\ & - \beta_2|\tilde{\eta}|^4 \sin^2 2\psi \sin^2(\phi_1 - \phi_2) + \theta_1|\eta|^2|\tilde{\eta}|^2 \\ & + \theta_2|\eta|^2|\tilde{\eta}|^2 [\cos^2 \psi \cos 2\phi_1 + \sin^2 \psi \cos 2\phi_2]. \end{aligned}$$

After a bit tedious calculation one obtains all of the stable solutions [14]:

1. $0 < \beta_2$

$$(\eta, \eta_1, \eta_2) = (a, \frac{b}{\sqrt{2}}e^{i\phi}, \pm i\frac{b}{\sqrt{2}}e^{i\phi}), \quad (9)$$

where,

$$a = \sqrt{-\frac{A_{A_1}(T)}{2\beta}}, b = \pm \sqrt{-\frac{A_E(T)}{2(\beta_1 - |\beta_2|)}},$$

and ϕ is arbitral here.

2. $\beta_2 < 0$

$$(\eta, \eta_1, \eta_2) = \begin{cases} (c, \pm id \cos \psi, \pm id \sin \psi), & \text{for } 0 < \theta_2 \\ (c, \pm d \cos \psi, \pm d \sin \psi), & \text{for } \theta_2 < 0, \end{cases} \quad (10)$$

where,

$$c = \sqrt{-\frac{A_{A_1}(T)}{2\beta}}, d = \sqrt{-\frac{A_E(T)}{2\beta_1}},$$

and ψ is arbitral. The degeneracy of ψ is lifted by taking into account the 6-th order terms for (η_1, η_2) as a weak perturbation [2]

$$\gamma_1(|\eta_1|^2 + |\eta_2|^2)^3 + \gamma_2(|\eta_1|^2 + |\eta_2|^2)|\eta_1^2 + \eta_2^2|^3 + \gamma_3|\eta_1|^2|3\eta_2^2 - \eta_1^2|.$$

The coupling terms between η and (η_1, η_2) are neglected here. Then,

$$\psi = \begin{cases} 0, \pi & (0 < \gamma_3) \\ \pm \frac{\pi}{2} & (\gamma_3 < 0). \end{cases} \quad (11)$$

From Eqs. (4), (6), (10) and (11), one can see that the two-dip state (anisotropic $s + id_{z^2-x^2}$ -wave state) is stable when $\beta_2, \gamma_3 < 0 < \theta_2$. On the other hand, it is hard to see how the four-dip state Eq. (5) can be stabilized in the present argument.

The gap structures for the other stable solutions (Eq. (9) and Eq. (10) for $\theta_2 < 0$) are inconsistent with the thermal conductivity measurement [5]. Furthermore, based on a consideration for the condensation energy within the weak coupling approach, it has been pointed out that the $s + id$ -wave state is energetically favored in $A_1 \oplus E$ combined representation [15].

From these considerations, we conclude that the two-dip state appears to be realized in the B-phase.

C. phase transition and symmetry breaking

Let us summarize the results in this section and try to describe the phase transition in the absence of the magnetic field.

Put the parameters

$$T_{A_1} = T_{c1} = 1.85K, T_E = T_{c2} = 1.75K, \quad (12)$$

and $\beta_2, \gamma_3 < 0 < \theta_2$ in the GL free energy Eq. (7). For simplicity, we take Eq. (8). Then, the stationary values of the order parameters in the A-phase ($T_{c2} < T < T_{c1}$) are

$$\eta = \sqrt{-\frac{A_{A_1}(T)}{2\beta}}, \eta_1 = \eta_2 = 0, \quad (13)$$

and in the B phase ($T < T_{c2}$)

$$\eta = \sqrt{-\frac{A_{A_1}(T)}{2\beta}}, \eta_1 = 0, \eta_2 = \pm i\sqrt{-\frac{A_E(T)}{2\beta_1}}. \quad (14)$$

From Eqs. (4), (13) and (14), one can see that the gap function in the A-phase has six dips along the [100], [010] and [001] directions (anisotropic s -wave state), and that in the B-phase there are two dips along the [010] direction (anisotropic $s + id_{z^2-x^2}$ -wave state). The result is consistent with the thermal conductivity measurement [5].

The gap function in the B-phase breaks the cubic crystal symmetry and also the time reversal symmetry. The consequence of this cubic symmetry breaking will be discussed in section IV. As a signal of the time reversal symmetry breaking, it is expected that a spontaneous magnetization be observed by the μ SR measurement [2].

III. SPECIFIC HEAT JUMP

In this section, we calculate the jumps of the specific heat at the two transition points $T_{c1} = 1.85K$ and $T_{c2} = 1.75K$ in Fig. 1 indicated by the specific heat measurement [4]. To fit the calculation to the experimental result the ratio of the coefficients of 4-th order terms in GL potential β/β_1 is obtained. The simplification Eq. (8) is used.

Let us introduce

$$\vec{\eta} = (\eta, \eta_1, \eta_2).$$

By using the stationary condition for the free energy Eq. (7)

$$0 = \frac{\partial F_{op}}{\partial \vec{\eta}}, \quad (15)$$

the specific heat is

$$\begin{aligned} C(T) &= C_0(T) - T \frac{\partial^2 F_{op}}{\partial T^2} \\ &= C_0(T) - T \left\{ \frac{\partial \vec{\eta}}{\partial T} \cdot \frac{\partial^2 F}{\partial \vec{\eta} \partial T} + c.c. \right\}, \end{aligned} \quad (16)$$

where $C_0(T)$ is the background specific heat. Let us define $\Delta C(T) = C(T) - C_0(T)$. Then, in the A-phase,

$$\Delta_A C(T) = \frac{T}{2\beta T_1^2}, \quad (17)$$

while in the B-phase,

$$\Delta_B C(T) = T \left(\frac{1}{2\beta T_1^2} + \frac{1}{2\beta_1 T_3^2} \right). \quad (18)$$

Therefore, the ratio of the jumps at the two transition points is

$$\frac{\Delta_B C(T_{c2}) - \Delta_A C(T_{c2})}{\Delta_A C(T_{c1})} = \frac{\beta T_{c1}}{\beta_1 T_{c2}} \quad (19)$$

The experimental result for this quantity is around 1 [4]. Then, from Eq. (12), one can obtain the ratio

$$\beta/\beta_1 \simeq 0.9. \quad (20)$$

IV. CUBIC SYMMETRY BREAKING IN B-PHASE

the B-phase gap breaks the cubic crystal symmetry T_h spontaneously. So, one can expect a crystal deformation with the cubic symmetry breaking. In this section, the strain-order parameter coupling is taken into account and thermal expansions and isothermal elastic constants are calculated [9]. In the B-phase, one obtains anisotropic results for these values. This comes from the spontaneous crystal symmetry breaking.

A. strain-orderparameter coupling

The GL potential which include the strain-order parameter coupling is [2],

$$\begin{aligned} F_{GL} &= F_{op} + F_{st-op} + F_{el}, \\ F_{st-op} &= -|\eta|^2 C_{A1} (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \\ &\quad - |\eta_1|^2 [C_{A1} (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \\ &\quad \quad + C_E (2\epsilon_{yy} - \epsilon_{zz} - \epsilon_{xx})] \\ &\quad - |\eta_2|^2 [C_{A1} (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \\ &\quad \quad - C_E (2\epsilon_{yy} - \epsilon_{zz} - \epsilon_{xx})] \\ &\quad - \sqrt{3} C_E (\eta_1 \eta_2^* + c.c.) (\epsilon_{zz} - \epsilon_{xx}) \\ &\quad - C_{AE} (\eta \eta_1^* + c.c.) (2\epsilon_{yy} - \epsilon_{zz} - \epsilon_{xx}) \\ &\quad - \sqrt{3} C_{AE} (\eta \eta_2^* + c.c.) (\epsilon_{zz} - \epsilon_{xx}), \\ F_{el} &= \frac{1}{2} \sum_{ijkl} c_{ijkl}^{(0)} \epsilon_{ij} \epsilon_{kl}, \end{aligned} \quad (21)$$

where $c_{ijkl}^{(0)}$ is the background elastic constants. Obviously, it is symmetric under the T_h symmetry.

Let us consider the amplitude of the strain. It is obtained by solving the equation

$$0 = \frac{\partial F_{GL}}{\partial \epsilon_{ij}},$$

We introduce the notation $\epsilon_{xx} = \epsilon_1, \epsilon_{yy} = \epsilon_2, \epsilon_{zz} = \epsilon_3, \epsilon_{xy} = \epsilon_4, \epsilon_{yz} = \epsilon_5, \epsilon_{zx} = \epsilon_6$. In the A-phase (see, Eq. (13)), one finds the isotropic result

$$\begin{aligned} \epsilon_1 = \epsilon_2 = \epsilon_3 &= -\frac{C_{A1}}{\lambda} \frac{A_{A1}(T)}{2\beta}, \\ \epsilon_4 = \epsilon_5 = \epsilon_6 &= 0, \end{aligned} \quad (22)$$

where $\lambda = c_{11}^{(0)} = c_{22}^{(0)} = c_{33}^{(0)}$. In B-phase (See, Eq. (14)), an anisotropy can be seen in the y direction:

$$\begin{aligned} \epsilon_3 = \epsilon_1 &= -\frac{C_{A1}}{\lambda} \frac{A_{A1}(T)}{2\beta} - \frac{C_{A1} + C_E}{\lambda} \frac{A_E(T)}{2\beta_1}, \\ \epsilon_2 &= -\frac{C_{A1}}{\lambda} \frac{A_{A1}(T)}{2\beta} - \frac{C_{A1} - 2C_E}{\lambda} \frac{A_E(T)}{2\beta_1}, \\ \epsilon_4 = \epsilon_5 = \epsilon_6 &= 0. \end{aligned} \quad (23)$$

It should be noted that the terms proportional to C_{AE} in Eq. (21) play no roles in the state Eq. (14).

B. thermal expansion

The presence of the strain can be measured by the thermal expansion which is definition by

$$\alpha_\mu = \alpha_\mu^{(0)} + \frac{\partial \epsilon_\mu}{\partial T}, \quad (24)$$

where $\mu = 1, \dots, 6$, and $\alpha_\mu^{(0)}$ is the background value. Define $\Delta \alpha_\mu = \alpha_\mu - \alpha_\mu^{(0)}$. Then, in the A-phase (See, Eq. (22)),

$$\begin{aligned} \Delta_A \alpha_1 = \Delta_A \alpha_2 = \Delta_A \alpha_3 &= -\frac{C_{A1}}{\lambda} \frac{1}{2\beta T_{c1}}, \\ \Delta_A \alpha_4 = \Delta_A \alpha_5 = \Delta_A \alpha_6 &= 0. \end{aligned} \quad (25)$$

In B-phase (See, Eq. (23)), the thermal expansion becomes anisotropic:

$$\begin{aligned} \Delta_B \alpha_3 = \Delta_B \alpha_1 &= -\frac{C_{A1}}{\lambda} \frac{1}{2\beta T_{c1}} - \frac{C_{A1} + C_E}{\lambda} \frac{1}{2\beta_1 T_{c2}}, \\ \Delta_B \alpha_2 &= -\frac{C_{A1}}{\lambda} \frac{1}{2\beta T_{c1}} - \frac{C_{A1} - 2C_E}{\lambda} \frac{1}{2\beta_1 T_{c2}}, \\ \Delta_B \alpha_4 = \Delta_B \alpha_5 = \Delta_B \alpha_6 &= 0. \end{aligned} \quad (26)$$

The thermal expansion along [100] direction has been measured [8], and two clear jumps are observed at T_{c1} and T_{c2} . The ratio of these two jumps is

$$\frac{\Delta_B \alpha_1 - \Delta_A \alpha_1}{\Delta_A \alpha_1} = \left(1 + \frac{C_E}{C_{A_1}}\right) \frac{\beta}{\beta_1} \frac{T_{c1}}{T_{c2}} \simeq 1.8. \quad (27)$$

From Eqs. (12) and (20), one can obtain a relation

$$C_E/C_{A_1} \simeq 0.9, \quad (28)$$

and estimate the ratio of jumps at the two transition points for the thermal expansion in the [010] direction

$$\frac{\Delta_B \alpha_2 - \Delta_A \alpha_2}{\Delta_A \alpha_2} = \left(1 - 2 \frac{C_E}{C_{A_1}}\right) \frac{\beta}{\beta_1} \frac{T_{c1}}{T_{c2}} \simeq -0.8. \quad (29)$$

This quantity has not been measured yet.

C. isothermal elastic constants

The isothermal elastic constant is

$$c_{\mu\nu} = \left(\frac{\partial^2 F_{GL}}{\partial \epsilon_\mu \partial \epsilon_\nu} \right)_T. \quad (30)$$

The small variation of the strain changes the amplitude of the order parameters as

$$\begin{aligned} \delta|\eta|^2 &= \frac{C_{A_1}}{2\beta} (\delta\epsilon_1 + \delta\epsilon_2 + \delta\epsilon_3), \\ \delta|\eta_2|^2 &= \frac{C_{A_1}}{2\beta_1} (\delta\epsilon_1 + \delta\epsilon_2 + \delta\epsilon_3) \\ &\quad - \frac{C_E}{2\beta_1} (2\delta\epsilon_2 - \delta\epsilon_3 - \delta\epsilon_1). \end{aligned} \quad (31)$$

By using the condition Eq. (15),

$$c_{\mu\nu} = c_{\mu\nu}^{(0)} + \left[\frac{\partial \vec{\eta}}{\partial \epsilon_\mu} \cdot \frac{\partial^2 F_{GL}}{\partial \vec{\eta} \partial \epsilon_\nu} + c.c. \right], \quad (32)$$

where $c_{\mu\nu}^{(0)}$ is the background elastic constant. Let us define $\Delta c_{\mu\nu} = c_{\mu\nu} - c_{\mu\nu}^{(0)}$. In A-phase,

$$\Delta_A c_{11} = \Delta_A c_{22} = \dots = \Delta_A c_{31} = -\frac{C_{A_1}^2}{2\beta}, \quad (33)$$

and the others are zero. In B-phase,

$$\begin{aligned} \Delta_B c_{33} &= \Delta_B c_{11} = \Delta_B c_{31} = -\frac{C_{A_1}^2}{2\beta} - \frac{(C_{A_1} + C_E)^2}{2\beta_1}, \\ \Delta_B c_{22} &= -\frac{C_{A_1}^2}{2\beta} - \frac{(C_{A_1} - 2C_E)^2}{2\beta_1}, \\ \Delta_B c_{23} &= \Delta_B c_{12} = -\frac{C_{A_1}^2}{2\beta} - \frac{(C_{A_1} + C_E)(C_{A_1} - 2C_E)}{2\beta_1}, \end{aligned} \quad (34)$$

and the others are zero. From Eqs. (20) and (28), one can estimate the ratios of jumps at two transition points of the elastic constants,

$$\begin{aligned} \frac{\Delta_B c_{11} - \Delta_A c_{11}}{\Delta_A c_{11}} &= \frac{\beta}{\beta_1} \left(1 + \frac{C_E}{C_{A_1}}\right)^2 \simeq 3.6, \\ \frac{\Delta_B c_{22} - \Delta_A c_{22}}{\Delta_A c_{22}} &= \frac{\beta}{\beta_1} \left(1 - 2 \frac{C_E}{C_{A_1}}\right)^2 \simeq 0.6, \\ \frac{\Delta_B c_{12} - \Delta_A c_{12}}{\Delta_A c_{12}} &= \frac{\beta}{\beta_1} \left(1 + \frac{C_E}{C_{A_1}}\right) \left(1 - 2 \frac{C_E}{C_{A_1}}\right) \\ &\simeq -1.4. \end{aligned} \quad (35)$$

In conclusion for this section, the thermal expansion and the elastic constant are isotropic in the A-phase, but anisotropic in the B-phase. To observe the anisotropy would serve as additional evidences for the phase transition and the spontaneous cubic symmetry breaking in the B-phase.

V. SUMMARY AND DISCUSSIONS

In summary, the multiple superconducting phases (A-phase and B-phase) in the skutterudite $\text{PrOs}_4\text{Sb}_{12}$ with cubic crystal symmetry T_h is discussed by using the phenomenological Ginzburg-Landau approach. The spin singlet pairing case is considered here. According to the thermal conductivity measurement [5], the gap function has within in the ab -plane four point-node-like structure (four dips) along the [100] and [010] directions on the Fermi surface in the A-phase, and two dips along the [010] direction in the B-phase. But the gap structure along the c -axis was unresolved. This problem is considered here.

Because of the absence of an anisotropy in H_{c2} [5], the superconductivity in A-phase appears to be the conventional state (anisotropic s -wave state). Then, the gap structure has the cubic symmetry (the A_1 representation) and leads to two additional dips along the c -axis. In the B-phase, a state without additional dips along the c -axis (anisotropic $s + id_{z^2-x^2}$ -wave state) is stabilized by the Ginzburg-Landau potential of the $A_1 \oplus E$ combined representation in a wide parameter region. On the other hand, it is hard to see that a state with two dips along c -axis is stabilized, since to obtain such a state requires a highly accidental mixing between the basis functions of the crystal symmetry T_h . Moreover, it has been shown that the $s + id$ -wave state is energetically favored in the $A_1 \oplus E$ combined representation based on the consideration for the condensation energy of each state within the weak coupling approach [15]. Hence it is natural to expect that the gap function in A-phase has a total of six dips along [100], [010] and [001] directions and while in the B-phase there are in total two dips along the [010] direction. The phase transition can be described by the Ginzburg-Landau potential.

The gap function in the B-phase breaks the cubic crystal symmetry T_h spontaneously. This symmetry breaking would cause anisotropic crystal strain and anisotropic

anomaly of the thermal expansion and the isothermal elastic constant could be observed .

The gap function in B-phase breaks the time reversal symmetry (See, Eqs. (4) and (6)). Then, the spontaneous magnetization around impurities is expected to be observed by the μ SR measurement [2]. The magnetization have not been detected yet. More accurate measurements are highly desired [7].

Another expected phenomenon in the B-phase is anomalous flux flow which comes from the domain formation [16], because the domain structure would exist in the B-phase since the stable state Eq. (6) is two-fold degenerate.

Additional phase transitions induced by uniaxial pressure may be possible in this superconductor. Such a transition could occur in a superconductor described by multicomponent order parameter [2].

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